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In Situ Studies of Nitridation of Zirconia (ZrO_2)

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The nitridation of an amorphous $ZrO_2 \cdot H_2O$ precursor with gaseous ammonia has been studied by in situ X-ray powder diffraction (temperature range 25−1100 °C), electron diffraction (temperature range 25−800 °C), and electron energy loss spectroscopy (EELS) using a transmission electron microscope equipped with an environmental cell (e-cell). The results show that under the conditions in the e-cell of a transmission microscope ($P_{NH_3} = 2$ Torr) a cubic nitrogen-containing phase is formed at 820 °C. This phase has low nitrogen content with no superstructure reflections, confirming the absence of anion/vacancy ordering. X-ray diffraction results under an ammonia partial pressure of 760 Torr show that at 1100 °C, 500 °C below the usual temperature for the tetragonal to cubic phase transition in zirconia, a cubic phase is formed that must be due to the incorporation of nitrogen into the anion lattice. On slow cooling from 1100 °C some superstructure reflections related to the fluorite structure have been observed, on account of the ordering of the anion/vacancies. The EELS data show that the color of the samples can be related to the overall nitrogen content in the samples; i.e., the color changes from green to yellow to white as the nitrogen content in the sample decreases.

Introduction

Zirconium oxide (ZrO_2) is one of the most studied materials due to its industrial applications as a ceramic material, oxygen sensor, electrolyte in fuel cells, etc. Pure ZrO_2 has a monoclinic structure at room temperature that transforms to a tetragonal structure (>1100 °C) and finally into a cubic structure (>1600 °C) upon heating. The 4% volume change due to the monoclinic to the tetragonal phase transformation results in formation of cracks, thus restricting its use to a much lower temperature.[1] As the metastable tetragonal and cubic ZrO_2 have improved mechanical and electrical properties, the effort has been concentrated on stabilizing cubic zirconia by cation substitution, e.g. MgO, CaO, Y_2O_3.[2,3] The tetragonal phase has been most commonly observed during crystallization[2,4−8] due to the surface strain present due to particle size effects.[9] Clearfield[4] first reported the presence of a cubic phase during crystallization and attributed it to the stabilization by residual (OH) groups. Later Garvie[5] reported it to be an error of measurement and proposed that the doublet of the tetragonal phase appears to be extinct due to particle size line broadening in the powder X-ray diffraction patterns. Recently, the metastable cubic phase (1−2 nm particle size) has been confirmed to form during the in situ study of crystallization of ZrO_2, which transformed to the tetragonal and finally to the monoclinic phase during electron beam heating.[6] An addition of 5−15% of Mn has been reported to stabilize the cubic structure for slightly larger crystal size (5−20 nm) and up to higher temperatures (850 °C).[7]

Besides the stabilization by cation substitution, attempts have been made to stabilize cubic zirconia by replacing oxygen through nitrogen in the anion sublattice.[10−13] The reported oxide−nitrides, with a general formula $ZrO_{2-2x}N_{4x/3}$, fall on the ZrO_2−Zr_3N_4 line of the phase diagram instead of the ZrO_2−ZrN line. These oxide−nitrides have been synthesized by heating ZrO_2 or a mixture of ZrO_2 and ZrN in N_2 or NH_3 at 1100 °C. These efforts have resulted in the formation of fluorite-related superstructures and an ordering of oxygen and nitrogen, and/or vacancies in the lattice have been assumed.[14] Examples are the structures of Zr_2ON_2 (γ), $Zr_7O_8N_4$ (β) $Zr_{14}O_{22}N_4$ (β') and incommensurate modulated structures of β', with lower nitrogen content (β'').[11] All of the β-phases crystallize in $R\bar{3}$ (or $P\bar{3}$) with the same lattice constant a and different values for c.[10] For the β''-phase, different modulations of the rhombohedral β-phase structure have been observed. All modulations are roughly along the $[001]_\beta$, with distances between

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2.667 and 4.3 times c_β. This ordering of vacancies is reported to have a negative effect on the ionic conductivity of these materials.[15] It has been suggested that the ordering of O/N may be the driving force for the vacancy ordering.[16] However, no O/N ordering was observed during the neutron diffraction studies of Zr_2ON_2.[17]

We have used in situ time- and temperature-resolved electron and x-ray diffraction in a vacuum and in a controlled atmosphere of dry NH_3 gas in order to understand the pathway of the nitridation reaction under different environmental conditions and to elucidate the existence of metastable phases.

Experimental Section

To obtain highly reactive starting materials, the precursor was prepared by dissolving $ZrOCl_2 \cdot 8H_2O$ (Aldrich; 99.99%) in the deionized water and precipitating $ZrO_2 \cdot H_2O$ with an excess of aqueous NH_3 following the reaction equation:

$$ZrOCl_2 \cdot H_2O + 2NH_3 \rightarrow ZrO_2 \cdot H_2O + 2NH_4Cl$$

The precipitates of $ZrO_2 \cdot H_2O$ (or $Zr(OH)_2$) were then washed in order to remove traces of NH_4Cl till the pH of the filtrate was approximately 7. The product was then dried at 120 °C for 48 h. Both in situ powder X-ray diffraction and electron microscopy were used in order to follow nitridation reaction. The thermogravimetric analysis indicated that one mole of H_2O was present in the sample.

(a) In Situ Powder X-ray Diffraction. Samples were heated to 1100 °C in a HDK S1 reaction chamber (Johanna Otto GmbH) fitted on a Siemens D5000 X-ray powder diffractometer both in a vacuum and in an atmosphere of ammonia (constant gas flow). Time- and temperature-resolved X-ray powder diffraction patterns were recorded in the 2θ range between 10° and 60° using a position sensitive detector with 6° aperture. Measurements were carried out during heating and cooling in order to determine the onset of structural transformations. Diffraction patterns were recorded every 12 min, at an interval of 100 °C up to 500 °C and every 50 °C thereafter up to 1100 °C during heating. The sample was isothermally heated at 1100 °C for 72 min, while still recording a pattern every 12 min. The diffraction patterns were recorded with a resolution of 25 °C/12 min during cooling.

(b) In Situ Transmission Electron Microscopy. For electron microscopy studies, samples were dry-loaded on 200 mesh Cu or Mo grids. A PHILIPS-430 transmission electron microscope operated at 300 kV, equipped with a differentially pumped environmental cell fitted between the objective pole pieces and a postprojector Gatan Imaging Filter (GIF), was used to study gas−solid interactions.[18] The samples were heated using a single-tilt PHILIPS heating holder in a vacuum as well as under a partial pressure of 2 Torr of dry NH_3. The selected area electron diffraction (SAED) patterns were recorded after every 100 °C up to 300 °C, after every 50 °C up to 450 °C, and every 25 °C up to 820 °C starting from room temperature. As our starting materials can also be heated by electron beam, the study was restricted to low-electron-dose SAED work. Time- and temperature-resolved SAED patterns were recorded for 8−10 crystals starting from room temperature. Electron energy loss spectra were recorded before and after the reaction without the gas flow to avoid the nitrogen signal from NH_3 interfering with analysis using the GIF with an energy resolution of 2.5−3 eV.

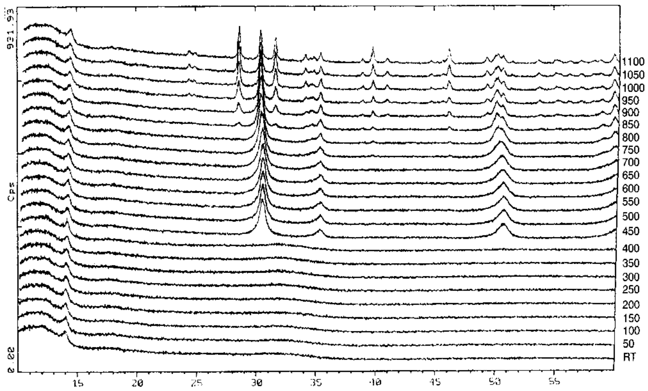

Figure 1. Time- and temperature-resolved powder X-ray diffraction patterns from $ZrO_2 \cdot H_2O$ showing the onset of the crystallization at 450 °C and successive phase transformations to the tetragonal (750 °C) and the monoclinic zirconia (900 °C).

Results from in Situ X-ray Diffraction

(a) The Thermal Decomposition of Amorphous $ZrO_2 \cdot H_2O$ under Vacuum (25−1100 °C). The samples were heated in a vacuum in order to understand the crystallization behavior of the precursor and distinguish it from the nitridation reaction. Time- and temperature-resolved powder X-ray diffraction patterns are shown in Figure 1. The amorphous precursor $ZrO_2 \cdot H_2O$ starts to crystallize at 450 °C in a cubic form. A splitting of $\{200\}_c$ reflection is observed at 800 °C, indicating the transformation to a tetragonal phase. Similarly, further splitting of X-ray diffraction lines confirms the transformation to a monoclinic phase at 900 °C, which is stable up to 1100 °C. As expected, no further changes were observed during the cooling of the sample.

(b) The Reaction of Amorphous $ZrO_2 \cdot H_2O$ with Ammonia. Figure 2 shows the time- and temperature-resolved X-ray diffractograms of the reaction of an amorphous precursor material $ZrO_2 \cdot H_2O$ and ammonia. It is clear from these diffraction patterns that the crystallization of a cubic phase started at 400 °C. This phase transformed into the tetragonal phase, which in turn transformed to the monoclinic phase at 800 °C. At 1100 °C, the monoclinic phase transformed back into the cubic phase (Figure 2b). The existence of the cubic phase, first observed at 400 °C, can be explained due to the particle size effect.[8,9] But the transformation of the monoclinic phase back to the cubic phase at 1100 °C is still 500 °C below the transformation point given in the phase diagram for zirconia[19] and must be due to the incorporation of nitrogen into the anion lattice. On cooling slowly to 800 °C, the observed superstructure reflections indicate the formation of a super lattice, most probably due to the anion/vacancy ordering. This formation of β'- and β''-phases agrees with the reported loss in the nitrogen content of the sample and also with a change in color from green to yellow to white. A similar change in color due to nitrogen incorporation has been reported recently for $Ca_{(1-x)}La_xTaO_{(2-x)}N_{(1+x)}$ compounds.[20]

From the ex situ experiments an electron diffraction powder pattern was found showing a modulated β''-phase with a modulation length of 4.67 times the c_β-

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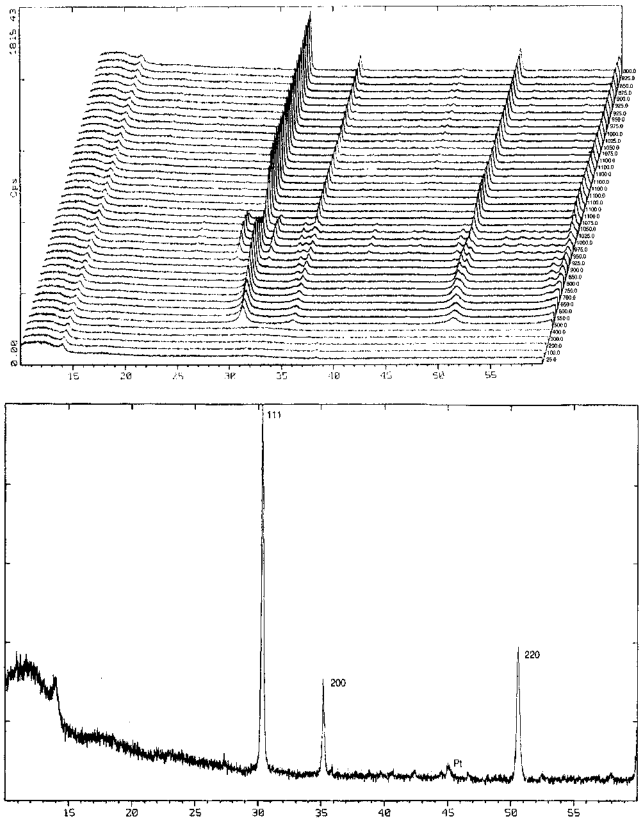

Figure 2. (a) The time- and temperature-resolved powder X-ray diffraction patterns from $ZrO_2 \cdot H_2O$, heated in NH_3, showing the onset of the crystallization of a cubic structure at 400 °C and successive phase transformation to the tetragonal (750 °C) and the monoclinic (900 °C) zirconia followed by the stabilization to the cubic phase at 1050 °C. (b) The powder X-ray diffraction pattern at 1100 °C showing the cubic phase formed during in situ heating experiment shown in Figure 2a. The Pt lines are from heating plate.

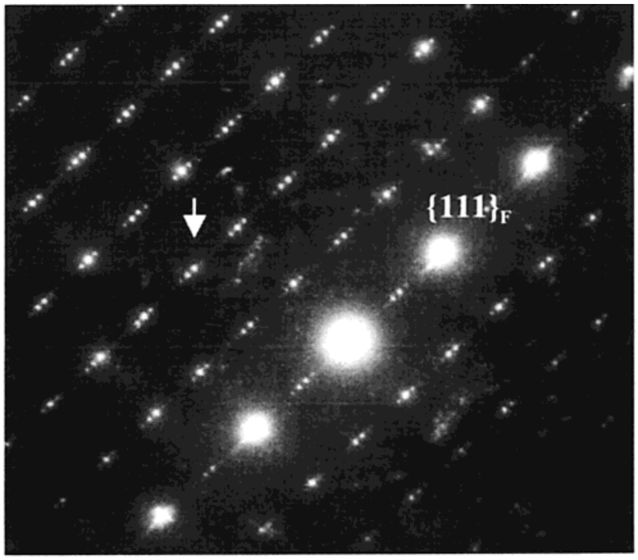

Figure 3. (a) SAED patterns of a $\langle\text{-}321\rangle_F$ zone and (b) a superstructure zone including a $\{111\}_F$ axis showing incommensurate modulation of the $Zr_{14}O_{22}N_4$ structure (β'').

axis (Figure 3). This might indicate an intergrowth phase of the β'-phase ($2c_\beta$) and the modulated phase with modulation length 2.67 or 8, as reported by van Tendeloo[21] and Lerch.[9]

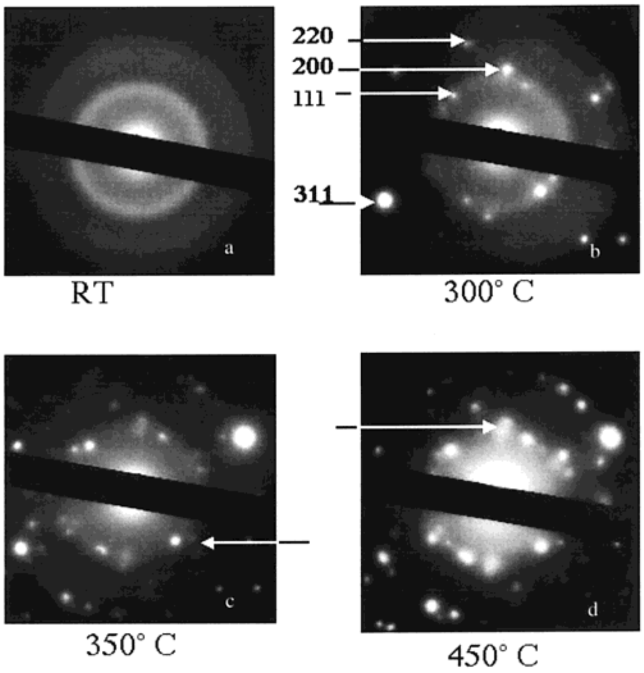

Figure 4. The selected area electron diffraction (SAED) patterns from $ZrO_2 \cdot H_2O$ sample showing (a) an amorphous diffraction pattern at room temperature that crystallizes into (b) a cubic structure at ~300 °C. After 1.5 h, (c) at 350 °C the diffraction pattern could be indexed as tetragonal zirconia. Upon further heating (d), extra reflections from monoclinic phase were observed.

Results from In Situ Electron Diffraction

(a) The Thermal Decomposition of Amorphous $ZrO_2 \cdot H_2O$ under vacuum 25−800 °C). To avoid electron beam heating, the samples were only observed in diffraction mode. SAED patterns of the starting material consisted of broad diffuse rings due to its amorphous nature (Figure 4a). No change in the diffraction patterns was observed up to 300 °C, confirming the absence of electron beam heating. At 300 °C, a few diffraction spots and rings were observed, indicating the beginning of the crystallization process. The nucleation rate was observed to be very high, and within a few seconds well-defined diffraction rings were observed (Figure 4b). The diffraction pattern could be indexed as that of cubic zirconia (Figure 4b) (Table 1).

In Figure 4c, a splitting of the $\{200\}_c$ reflections, observed as the temperature was increased to 350 °C, confirmed the beginning of the transformation into the tetragonal phase (Table.1). The appearance of new reflections upon further heating at 450 °C indicated the beginning of the transformation into the monoclinic structure (Figure 4d). Although some of the observed *d* spacings are common for all the three known phases within the error margins for electron diffraction data (Table 1), the following trends clearly confirm the phase transformation:

(1) The first observed *d* spacing (2.92 Å) increases gradually as expected from reported X-ray diffraction data.

(2) Extra reflections due to the splitting of $\{200\}_c$ and $\{111\}_c$ diffraction rings appeared as the sample was heated, which confirmed the phase transformations.

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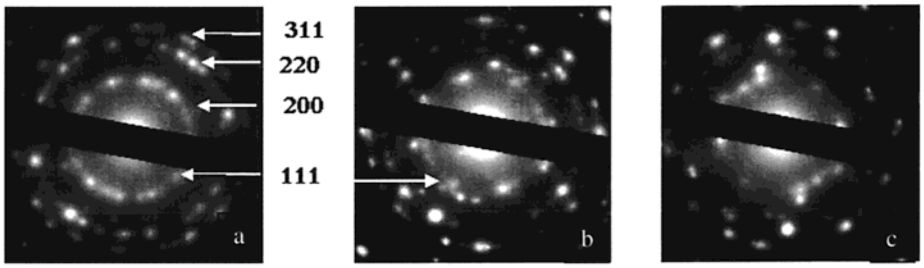

450 °C 475 °C 820 °C

Figure 5. A sequence of SAED patterns recorded during the heating of $ZrO_2{\cdot}H_2O$ sample in ~2 Torr of NH_3 showing (a) crystallization of a cubic structure at 450 °C that (b) transformed into a tetragonal structure at 475 °C. The extra reflections belonging to the tetragonal structure are marked with arrows. (c) The tetragonal structure transformed into a cubic structure upon further heating due to the N substitution in the lattice.

Table 1. Some of the Observed *d* Spacing as Measured from SAED Patterns for the Sample Heated in Vacuum and Their Indices

d_{obs} (Å)[a] 300 °C	d^b	*hkl* cubic	d_{obs} (Å) 350 °C	*d*	*hkl* tetragonal	d_{obs} (Å) 500 °C	*d*	*hkl* monoclinic
2.92	2.93	111	3.03	2.995	101	3.11	3.16	111
						2.80	2.839	111
2.6	2.66	200	2.67	2.635	002	2.61	2.620	002
			2.59	2.574	110			
1.82	1.801	220	1.97	1.841	112	2.23	2.2131	211
						1.91	1.991	211
1.51	1.534	311	1.60	1.582	103			
			1.55	1.555	211	1.61	1.6483	031
1.44	1.471	222	1.49	1.497	202	1.56	1.5819	222

[a] $d_{obs} = d$ spacings measured from SAED patterns. [b] $d = d$ spacing from JCPDS files.

Table 2. Some of The Observed *d* Spacing as Measured From SAED Patterns for the Sample Heated in NH_3 and Their Indices

d_{obs}(Å)[a] 425 °C	d^b	*hkl* cubic	d_{obs} (Å) 450 °C	*d*	*hkl* tetragonal	d_{obs} (Å) 820 °C	*d*	*hkl* cubic
2.92	2.93	111	2.96	2.995	101	2.92	2.93	111
2.5	2.66	200	2.63	2.635	200	2.67	2.66	200
			2.48	2.574	110			
1.78	1.801	220	2.06	2.134	102	1.76	1.801	220
			1.78	1.841	200			
1.52	1.534	311	1.51	1.555	211	1.55	1.534	311
			1.41	1.497	202	1.47	1.471	222
1.24	1.27	400	1.27	1.287	220			
			1.23	1.24	104			
1.15	1.167	331						

[a] $d_{obs} = d$ spacings measured from SAED patterns. [b] $d = d$ spacing from JCPDS files.

From our observations it was not possible to rule out the presence of two or more phases in any of the observed diffraction patterns, but for the present study, it was not important to determine the rate of transformation but to explore the reaction path under various environmental conditions, especially during crystallization. Except for increased sharpness of diffraction spots, no other changes were observed in the SAED patterns during 30 min of isothermal heating either at 300 °C or at 350 °C. The monoclinic structure was found to be stable during 1.5 h of heating at 750 °C.

(b) The Reaction of Amorphous $ZrO_2{\cdot}H_2O$ with Ammonia. Another part of the precursor sample was then heated under an atmosphere of ultrapure dry NH_3 gas (AIRCO, Electronic Gases, The BOC Group Inc.) using the environmental cell (partial pressure $P_{NH_3} =$ 2 Torr). In the beginning, a broad diffuse ring pattern similar to the one shown in Figure 4a was observed. The crystallization was observed to start at 450 °C and the first phase observed was indexed as cubic (Figure 5a).

The higher temperature of crystallization (450 °C in NH_3 instead of 300 °C in a vacuum) may be due the difference in gas pressure. At 475 °C, extra reflections were observed due to the cubic to tetragonal phase transformation (marked by arrows in Figure 5b). Upon further heating, spots on the ring pattern began to become sharper (Figure 5c), indicating an increased level of crystallinity. At 820 °C, the extra reflections from the tetragonal structure disappeared again and a cubic pattern was observed that was found to remain unchanged upon cooling. The diffraction rings are less diffuse in Figure 5c than in Figure 5a, indicating the larger particle size at higher temperature as expected. No monoclinic phase was observed during these studies. But the presence of a cubic structure at 820 °C for large particle size is again an indication of the nitridation reaction.

The measured *d* spacings were observed to have similar trends as observed for the sample heated in a vacuum (Table 2). The first observed *d* spacing changed from 2.92 to 2.96 Å and then back to 2.92 Å. The extra reflections belonging to the tetragonal structure disappeared, confirming the formation of a cubic structure. As a cubic oxide phase should not be stable at these temperatures, it must be stabilized by N substitution in the lattice.

To confirm the nitridation reaction, the electron energy-loss spectrum was recorded after stopping the gas flow in order to rule out the presence of the N-edge from NH_3 (Figure 6). A small hump at 400 eV, indicating the presence of N, was observed along with Zr, and O.

Discussion

The phase transformation reaction of ZrO_2 during crystallization in a vacuum by electron diffraction can

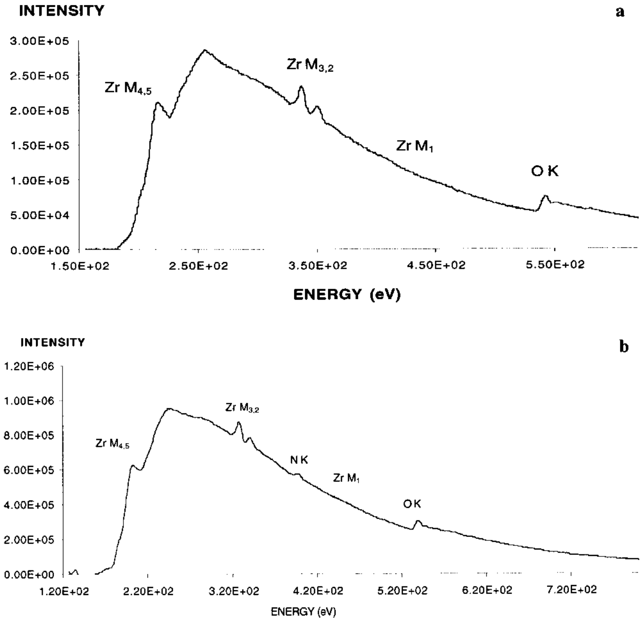

Figure 6. Electron energy-loss spectra (EELS) recorded (a) after the reaction at room temperature and in a vacuum (b) from pure ZrO_2 sample.

Table 3. Observed Transition Temperatures for $ZrO_2{\cdot}xH_2O$ (amorphous) → ZrO_2 (cubic particle size stabilized) → ZrO_2 (t) → ZrO_2(m) → ZrO_2 (cubic nitrogen stabilized) Observed under Different Environmental Conditions

	electrons		X-rays	
temp	25−850 °C	25−850 °C	25−1100 °C	25−1100 °C
pressure	$P_{NH_3} = 2$ Torr	vacuum	$P_{NH_3} = 760$ Torr	$P_{N_2} = 760$ Torr
cubic	450 °C	300 °C	450 °C	450 °C
tetragonal	475 °C	350 °C	750 °C	750 °C
monoclinic		450 °C	925 °C	900 °C
cubic	820 °C		1050 °C	

be written as

$$\text{amorphous} \rightarrow \text{cubic (300 °C)} \rightarrow \text{tetragonal (350 °C)} \rightarrow \text{monoclinic (450 °C)}$$

Our results are in agreement with the previous reports[5,9] for transformation up to the monoclinic phase, as we were not able to go to higher temperatures due to instrumental constraints. During this study, the presence of spots on diffraction rings observed indicate that the crystalline domain size for the cubic phase is larger than previously reported under electron beam heating conditions.[6] This can be due to the difference in heating rates by electron beam and by furnace heating. Also, the measured temperature for the advent of crystallization by electron diffraction is lower than the one observed by in situ X-ray diffraction. This nonconformity can be attributed to the fact that electron diffraction is more sensitive to the advent of crystallization than X-ray diffraction due to the smaller volume of the sample. In other words, the diffracting area used for electron diffraction is much smaller than the one used for X-ray diffraction. SAED patterns from the unexposed areas were also recorded to rule out the effect of electron beam heating.

The in situ study of the nitridation of $ZrO_2{\cdot}H_2O$ precursors in an e-cell transmission electron microscope shows that a cubic structure can be stabilized by N substitution in the lattice at 820 °C (see Table 3). No super-lattice reflections indicating the anion/vacancy ordering in the structure were observed during these studies. The phase transformation observed during crystallization in NH_3 in the e-cell TEM by electron diffraction can be written as

$$\text{cubic (450 °C)} \rightarrow \text{tetragonal (475 °C)} \rightarrow \text{cubic (820 °C)}$$

The amount of N observed by EELS in the cubic phase formed at 820 °C was quite low. Preliminary quantitative N/O atomic ratios were obtained by taking a ratio of the background subtracted N_K-edge and O_K-edge intensities integrated over a 50 eV window and adjusting them to the theoretical ionization cross-sections for respective edges. The N/O atomic ratio for the cubic phase was found to be 0.055 compared to 0.075 for the oxy−nitride phase obtained by ex situ reaction (shown Figure 3). The theoretical value for the β' ($Zr_{14}O_{22}N_4$) phase is 0.182, and β' is supposed to have a lower nitrogen content than β'. Although the difference in observed and theoretical value here could be due to the fact that the phase reported is a defect structure instead of a pure phase, we also know that the error in these measurements is high due to the overlap of Zr_M and N_K lines in the spectra. Better measurements using internal standards are needed for higher accuracy.

The X-ray diffraction results agree with the literature reports that nitrogen is incorporated into ZrO_2 at 1000−1100 °C ($P_{NH_3} = 760$ Torr).[10−13] The cubic phase formed at 1100 °C transformed to the fluorite related β structures of the zirconium oxide−nitride system on cooling, with an assumed anion and vacancy ordering are formed.

Since this ordering is decreasing the ionic conductivity of the material, it was important to stabilize a cubic zirconia phase, in this case by a statistical vacancy distribution. Our in situ electron diffraction results confirm that it is possible to obtain an N-stabilized cubic phase at 820 °C, which has the required statistical anion/vacancy distribution.

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